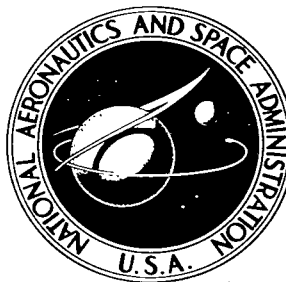


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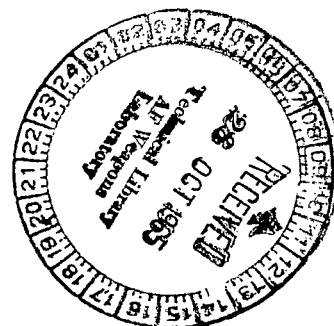


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PARTIAL WAVE CALCULATION OF THE DIATOMIC MOLECULE $(\text{HeH})^{++}$

by Harris Rabinovich

*Goddard Space Flight Center
Greenbelt, Md.*





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SUMMARY

The solutions to the Schrödinger equation for the diatomic molecule $(\text{HeH})^{++}$ in the Born-Oppenheimer approximation have been expanded in a series of partial waves and radial equations have been derived. These radial equations have been solved numerically for the first three orders of approximation and the energy eigenvalues and wavefunctions have been obtained for seven different Σ states at various values of the internuclear separation. The numerical wavefunctions have been used to calculate dipole transition integrals and dipole moments.

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INTRODUCTION

This paper contains an approximate calculation of the eigenvalues, eigenfunctions, and dipole transition integrals of the diatomic molecule $(\text{HeH})^{++}$ in the Born-Oppenheimer approximation. The method involves expanding the molecular wavefunctions in a series of partial waves about the charge center of the molecule. Although this approach is capable of yielding extremely precise results, this study was carried out with the intention of investigating how rapidly various orders of the approximation converge to the exact results and to what extent these approximate results display the qualitative features of the physics. This particular calculation is interesting because although previous calculations exist they are all restricted to $(\text{H}_2)^+$ which is homonuclear, whereas $(\text{HeH})^{++}$ is, of course, heteronuclear (References 1, 2, and 3). In addition, a number of new results are presented. These include the approximate eigenvalues of two Σ -states, the dipole moments for these states and others, and a large number of dipole transition integrals.

THEORY

The partial wave theory is a particular form of single center expansion. In this case the charge center is chosen as the origin and the wave function is expanded about this point. The motivation for this choice of origin is simply the fact that the forces are strictly Coulombic and the charge center is the point on the z -axis (taken as the internuclear axis) which has the greatest dynamical symmetry with respect to the potential. For example, when the electron is far from the nuclei, the nuclei behave like a single particle of charge $+3$ located at the charge center.

If A and B denote the helium and hydrogen nuclei, respectively, then in the Born-Oppenheimer approximation the Hamiltonian can be written as

$$H = -\nabla^2 - \frac{4}{r_A} - \frac{2}{r_B} + \frac{4}{R_{AB}} \quad (1)$$

(Here, and throughout this paper, lengths are in Bohr radii (0.529\AA) and energies in rydbergs (13.605 eV)). Having defined the origin and the z -axis, the next step is to expand the cosine law form of the electronic potentials in a series of Legendre polynomials about the charge center. This yields

$$H = -\nabla^2 - \sum_{j=0}^{\infty} V_j P_j(\cos \theta) + \frac{4}{R_{AB}} \quad (2)$$

where

$$V_j = \frac{\left[\left(-\frac{1}{2}\right)^j + 4 \right] r^j}{\left(\frac{1}{3} R_{AB}\right)^{j+1}} \quad r < \frac{1}{3} R_{AB} \quad (3)$$

$$V_j = \frac{2(-r)^j}{\left(\frac{2}{3} R_{AB}\right)^{j+1}} + \frac{4\left(\frac{1}{3} R_{AB}\right)^j}{r^{j+1}} \quad \frac{2}{3} R_{AB} > r > \frac{1}{3} R_{AB} \quad (4)$$

$$V_j = \frac{[2(-2)^j + 4] \left(\frac{1}{3} R_{AB}\right)^j}{r^{j+1}} \quad r > \frac{2}{3} R_{AB} \quad (5)$$

Except where specifically noted all the energy eigenvalues given include the internuclear potential.

The partial wave theory (Reference 1) starts with the expansion of the wave function in an infinite series of partial waves. For a given magnetic state, M , such an expansion is

$$\psi_M = \sum_{\ell} \Phi_{\ell}(r) Y_{\ell M}(\Omega) \quad (6)$$

If we insert Equation 6 into the Schrödinger equation and integrate over the angular variables, the result is an infinite set of coupled second-order differential equations:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + E + \frac{4}{R_{AB}} \right] \Phi_{\ell}(r) + \sum_m \sum_n \left(\frac{4\pi}{2n+1} \right)^{1/2} V_m C_{\ell mn}^{\text{MOM}} \Phi_n(r) = 0 \quad (7)$$

$C_{\ell mn}^{\text{MOM}}$ is simply an integral of the product of three spherical harmonics:

$$C_{\ell mn}^{\text{MOM}} = \int [Y_{\ell M}(\Omega) Y_{m0}(\Omega) Y_{nM}(\Omega)] d\Omega \quad (8)$$

Up to this point the solutions are exact. The approximation consists of replacing the infinite series of partial waves with a finite number of partial waves. Convergence of successive orders of the approximation is insured by the presence of the centrifugal barrier, $-\ell(\ell + 1)/r^2$, which depresses the magnitude of higher angular momentum terms in the region of the interaction (Reference 1). It can easily be shown that the variational determination of the $\Phi_\ell(r)$'s is equivalent to solving the set of equations

$$\int Y_{\ell M}^*(\Omega) H \psi_M d\Omega = E \Phi_\ell(r), \ell = 0, 1, \dots, L. \quad (9)$$

This is true for any order of the approximation. As a result the integral,

$$\int (\psi^* H \psi) dr, \quad (10)$$

will be a minimum for the ground state and an extremum for any excited state. Since the eigenfunctions of a particular order are the eigenfunctions of a Hermitian operator they are orthogonal as long as the eigenvalues are nondegenerate. The wave function for the p th order approximation contains $p + 1$ terms and yields a set of $p + 1$ coupled differential equations for each of the three regions of configuration space. The zeroth-order approximation corresponds to approximating the two separate Coulomb potentials by a truncated Coulomb potential of charge $+3$ located at the charge center. This approximation is pictured in Figure 1.

Several important properties of the approximate calculation can be deduced by examining the radial equations. For simplicity we will discuss the first order approximation. The first order wavefunction for Σ states is

$$\psi = \frac{\Phi_0(r)}{r} Y_{00} + \frac{\Phi_1(r)}{r} Y_{10}. \quad (11)$$

From Equation 9 we get a pair of coupled differential equations for each of the three regions of configuration space. In the united atom limit, $R_{AB} \rightarrow 0$, the situation is described by the pair of equations which are valid for $r > 2/3 R_{AB}$. At the limit, this pair of equations reduces to radial parts of the Schrödinger equation for the $\ell = 0$ and $\ell = 1$ states of the doubly ionized lithium atom. Hence the first-order approximation excludes all solutions which do not correspond to either s or p states in the

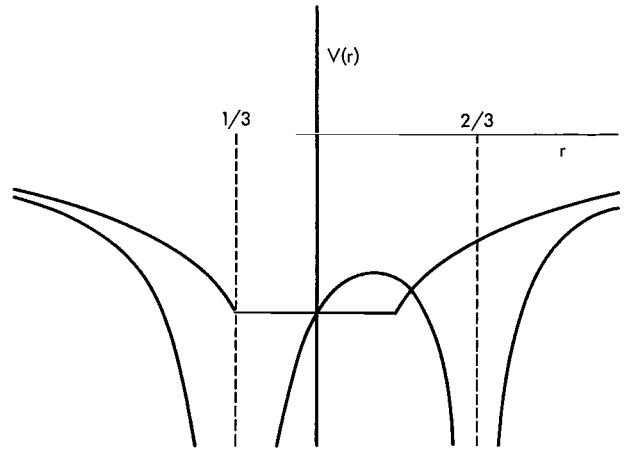


Figure 1—Exact Coulomb potential and the zeroth-order approximation for $R_{AB} = 1$.

united-atom limit. Therefore, a molecular d-state, united-atom designation, will be excluded in first-order, and in order to calculate it a second-order calculation is necessary. Infinite separation of the nuclei produces a situation in which the equations valid for $r < 1/3 R_{AB}$ are significant. In this limit the equations reduce to the radial portion of the Schrödinger equation for the free electron with either zero or unit angular momentum. At this point any calculation which uses a finite approximation yields incorrect results since the actual situation corresponds to either an alpha particle and a hydrogen atom or a singly ionized helium atom and a proton.

The differential equations which were derived in the previous paragraphs have been solved numerically. The method is an iterative procedure which involves integrating outward from the origin, while simultaneously integrating inward from some suitably chosen large value of the radius. At some intermediate value of the radius the solutions and their derivatives are matched. This technique was designed by L. Fox and is described in the appendix of a paper by Cohen and Coulson (Reference 2) and in a separate article by Fox (Reference 4). The calculations were performed on the IBM 7094 computer at the Theoretical Division of the Goddard Space Flight Center.

RESULTS

Calculations have been performed for six Σ states of the molecule. In the united-atom designation they are the $1s\sigma$, $2p\sigma$, $2s\sigma$, $3p\sigma$, $3d\sigma$ and $3s\sigma$ states. In the separated atom designation these same states correspond to the $\sigma(1s)He^+$, $\sigma(1s)H$, $\sigma(2s, 2p_z)He^+$, $\sigma(2s, 2p_z)H$, $\sigma(2s, 2p_z)He^+$, and $\sigma(3s, 3p_z, 3d_z)He^+$ states respectively. Table 1 contains the complete results of the eigenvalue calculations. Results for those Σ states which have been calculated exactly are included (Reference 5). Figure 2 is a graph of the potential energy of the ground state as a function of R_{AB} . The minima which appear in the potential energy curve in this case are spurious. Since the approximation reduces to a free-electron Hamiltonian for infinite separation, as described previously, any state which has a negative potential energy will show a minimum in its potential energy curve (Reference 1). The convergence of succeeding orders of the approximation is quite apparent. Figures 3 and 4 are graphs of the electron energy of the first five excited sigma states. The nuclear repulsion has been removed in order to show certain features. Notice that all states converge to their proper united-atom limits.

On the surface we might be tempted to test the results of these eigenvalue calculations with the provisions of the Hylleraas-Undheim theorem (Reference 6). This theorem establishes certain inequalities between the eigenvalues of successive orders of approximation of a variational calculation which is very similar to this one. In the Hylleraas-Undheim calculation the wave function is expanded in a complete set of functions with undetermined coefficients. The approximation consists of using a finite number of these functions and performing the variation on their coefficients. Hylleraas and Undheim show that if the eigenvalues of any order h are numbered calling the ground state E_0 , the first excited state E_1 , and the rest accordingly, then, $E_n^{(h)} \geq E_n^{(h+1)} \geq E_{n-1}^{(h)}$. The second order $3p\sigma$ and $3d\sigma$ eigenvalues violate the theorem between $R_{AB} = 1.5$ and $R_{AB} = 3$. However, this calculation satisfies conditions which are only similar and not identical to those of the Hylleraas-Undheim theorem. The difference is that in order to prove the inequalities between the eigenfunctions,

Table 1
Energy Eigenvalues.

R_{AB}	State	Zeroth Order	First Order	Second Order	Exact
0.25	1s σ	7.7871	7.7692	7.7365	7.7327
	2p σ		13.7129	13.7128	13.7125
	2s σ	13.8513	13.8491	13.8451	13.8446
	3p σ		14.9892	14.9891	
	3d σ			14.9984	14.9984
	3s σ	15.0303	15.0297	15.0285	
0.50	1s σ	0.8488	0.7815	0.6868	0.6689
	2p σ		5.6121	5.6109	5.6045
	2s σ	5.9970	5.9899	5.9784	5.9761
	3p σ		6.9617	6.9612	
	3d σ			6.9935	6.9935
	3s σ	7.0750	7.0730	7.0695	
0.75	1s σ	-0.9424	-1.0772	-1.2300	-1.2694
	2p σ		2.8250	2.8187	2.7870
	2s σ	3.4598	3.4463	3.4283	3.4232
	3p σ		4.2673	4.2652	
	3d σ			4.3184	4.3181
	3s σ	4.4492	4.4453	4.4400	
1.00	1s σ	-1.5831	-1.7895	-1.9952	-2.0667
	2p σ		1.4065	1.3915	1.3233
	2s σ	2.2359	2.2157	2.1924	2.1838
	3p σ		2.9202	2.9156	
	3d σ			2.9728	2.9716
	3s σ	3.1512	3.1456	3.1386	
2.00	1s σ	-1.8895	-2.3257	-2.6955	-3.0244
	2p σ		-0.4486	-0.4876	-0.6903
	2s σ	0.5385	0.4971	0.4551	0.4258
	3p σ		0.9737	0.9654	
	3d σ			0.8911	0.8575
	3s σ	1.2533	1.2423	1.2309	
3.00	1s σ	-1.6717	-2.2044	-2.6586	-3.3376
	2p σ		-0.7463	-0.7849	-1.0243
	2s σ	0.0612	0.0068	-0.0634	-0.1101
	3p σ		0.3924	0.3924	
	3d σ			0.1625	0.0176
	3s σ	0.6551	0.6403	0.6223	
4.00	1s σ	-1.4584	-2.0094	-2.4931	-3.5012
	2p σ		-0.7701	-0.8028	-1.0622
	2s σ	-0.1358	-0.1987	-0.3152	-0.3620
	3p σ		0.1286	0.1428	
	3d σ			-0.1463	-0.4137
	3s σ	0.3741	0.3559	0.3262	

the Hylleraas-Undheim theorem is restricted to a fixed set of basis functions, whereas in this calculation the basis functions, the $\Phi_l(r)$'s, change in each order of approximation. Empirically, a modified form of the Hylleraas-Undheim theorem appears to hold; namely, that $E_n^{(h)} \geq E_n^{(h+1)}$, provided one interprets the n 's correctly. Since the approximate energy curves in the same order

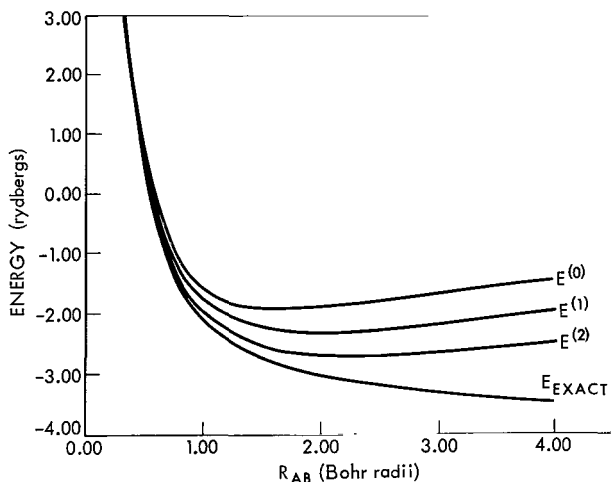


Figure 2— $1s\sigma$ electron energies versus R_{AB} . $E^{(2)}$ is the energy for the second-order approximation, etc.

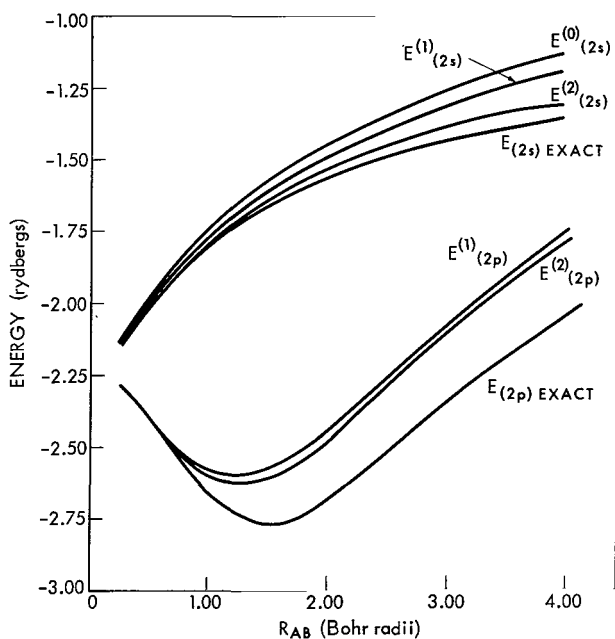


Figure 3— $2p\sigma$ and $2s\sigma$ electronic energies versus R_{AB} . $E^{(2)}$ is the energy for the second-order approximation, etc.

approximation may cross each other, the n th eigenvalue may refer to different spectral terms for different values of R_{AB} . For instance at $R_{AB} = 1$ in the second order approximation the $3p\sigma$ state lies lower than the $3d\sigma$ state and corresponds to E_3 , the third excited state, while the $3d\sigma$ state corresponds to E_4 , the fourth excited state. At $R_{AB} = 4$, the $3d\sigma$ state lies below the $3p\sigma$ state and corresponds to E_3 while the $3p\sigma$ state corresponds to E_4 . This results from the fact that the second order $3p\sigma$ and $3d\sigma$ states cross each other at R_{AB} slightly less than 2. By interpreting the n 's in this manner the condition that $E_n^{(h)} \geq E_n^{(h+1)}$ is fulfilled for all calculated results.

Dipole transition integrals were calculated using both the dipole length, Equation 12, and

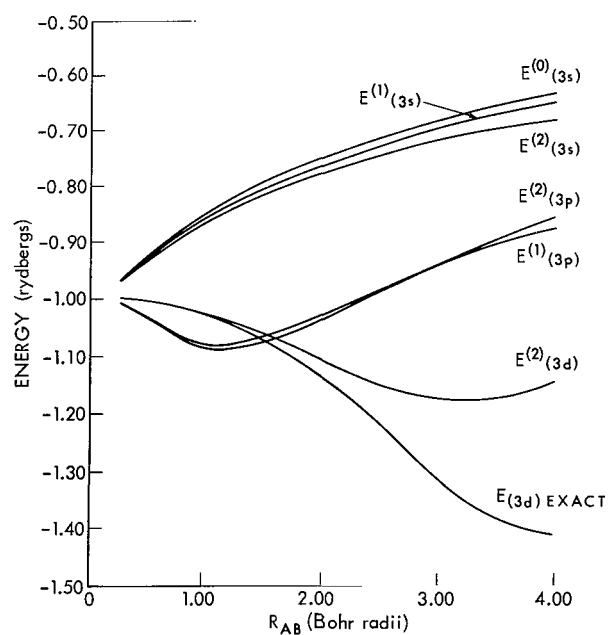


Figure 4— $3p\sigma$, $3d\sigma$, and $3s\sigma$ electronic energies versus R_{AB} . $E^{(2)}$ is the energy for the second-order approximation, etc.

the dipole velocity, Equation 13, formulations:

$$Q = \int \psi_a^* \hat{r} \psi_b d\tau \quad (12)$$

and

$$Q = \frac{2}{(E_a - E_b)} \int \nabla \psi_a^* \psi_b d\tau = - \frac{2}{(E_a - E_b)} \int \psi_a^* \nabla \psi_b d\tau \quad (13)$$

Table 2 includes both the approximate and exact (References 7 and 8) values of the dipole integrals. The dipole velocities were calculated using both forms of Equation 13 and all values agree within 0.5%. Figures 5, 6, and 7 depict the $2p\sigma$ - $2s\sigma$, $2p\sigma$ - $3d\sigma$, and the $1s\sigma$ - $3d\sigma$ transitions. If $\psi_a = \psi_b$ in Equation 12 then the z th component of this integral is the dipole moment. Table 3 contains a list of the approximate and exact dipole moment calculations (References 9 and 10). The dipole moment of the $2p\sigma$ and $3p\sigma$ states is measured with respect to the proton and the dipole moment of the remaining states is measured with respect to the alpha particle. The signs in Table 3 refer to the vector direction of the dipole moment and are to be interpreted in the normal sense. Figures 8 and 9 are graphs of the dipole moment for the $1s\sigma$ and $2p\sigma$ states.

We shall discuss all the calculations simultaneously so as to unify the discussion. This is particularly easy since the discrepancy between the exact and approximate results is due to a single cause, namely, the attempt to use a finite number of terms of the potential expansion about the charge center in place of the exact electronic potentials. For small internuclear separations, the electronic Coulomb potential wells coalesce and they can be approximated easily. Even the zeroth-order calculations are good, although in zeroth order the potential approximation is only a truncated Coulomb potential. As the internuclear separation increases the Coulomb potential wells separate and we are faced with trying to approximate the singularities of the two separate wells. In the higher order approximations the approximate potential possesses kinks which represent the singularities. However as R_{AB} increases, the magnitudes of the kinks decrease and they become poorer approximations to the singularities. Finally, as we stated previously, our approximate equations describe a free electron, whereas we really have an alpha particle and a hydrogen atom, or a singly ionized helium atom and a proton. This situation can be improved by using a greater number of terms to approximate the potential. The real question is, to what extent do the approximate results correspond to the exact results. The energy eigenvalues are within 6% of the exact values up to $R_{AB} = 1$ in the second-order approximation. This 6% discrepancy is for the ground state and represents the largest error at this point. The energy eigenvalues of the excited states are more accurate because these states have their maximum probability density in regions where the potentials are small and well represented. As a result the integral of the potential energy and its concomitant error are both reduced in magnitude.

In general one expects that increasing the order of approximation leads to a better representation of the potential and would extend the range of R_{AB} which produced valid results. This is

Table 2

Dipole Transition Integrals.

Transition	R_{AB}	1st Order Dipole Length	1st Order Dipole Velocity	2nd Order Dipole Length	2nd Order Dipole Velocity	Exact Value
$1s\sigma-2p\sigma$	0.00					0.248
	0.25	0.290	0.293	0.289	0.289	0.289
	0.50	0.356	0.376	0.360	0.359	0.360
	0.75	0.412	0.463	0.427	0.423	
	1.00	0.450	0.539	0.474	0.464	0.474
	2.00	0.443	0.681	0.488	0.441	0.417
	3.00	0.355	0.690	0.425	0.350	0.263
	4.00	0.280	0.685	0.386	0.294	0.168
$1s\sigma-2s\sigma$	0.00					0.000
	0.25	0.017	0.017	0.017	0.017	0.017
	0.50	0.036	0.037	0.038	0.038	0.038
	0.75	0.058	0.061	0.063	0.062	0.063
	1.00	0.080	0.087	0.089	0.088	0.092
	2.00	0.163	0.176	0.192	0.187	0.181
	3.00	0.224	0.228	0.293	0.301	0.217
	4.00	0.295	0.258	0.378	0.432	0.231
$1s\sigma-3p\sigma$	0.00					.050
	0.25	0.108	0.109	0.108	0.108	
	0.50	0.110	0.119	0.114	0.113	
	0.75	0.099	0.118	0.106	0.105	
	1.00	0.082	0.110	0.091	0.088	
	2.00	0.051	0.104	0.051	0.039	
	3.00	0.057	0.135	0.044	0.021	
	4.00	0.072	0.175	0.050	0.013	
$1s\sigma-3d\sigma$	0.00					0.000
	0.25			0.003	0.003	0.003
	0.50			0.009	0.009	0.009
	0.75			0.020	0.019	0.019
	1.00			0.036	0.035	0.035
	2.00			0.125	0.143	0.157
	3.00			0.146	0.211	0.258
	4.00			0.048	0.157	0.282
$1s\sigma-3s\sigma$	0.00					0.000
	0.25	0.007	0.007	0.007	0.007	
	0.50	0.016	0.016	0.016	0.016	
	0.75	0.025	0.027	0.027	0.027	
	1.00	0.034	0.038	0.038	0.037	
	2.00	0.070	0.076	0.079	0.076	
	3.00	0.097	0.099	0.111	0.111	
	4.00	0.119	0.111	0.131	0.144	

Table 2 (continued)

Dipole Transition Integrals.

Transition	R_{AB}	1st Order Dipole Length	1st Order Dipole Velocity	2nd Order Dipole Length	2nd Order Dipole Velocity	Exact Value
$2p\sigma-2s\sigma$	0.00					1.000
	0.25	0.977	0.972	0.977	0.972	0.977
	0.50	0.895	0.899	0.895	0.889	0.891
	0.75	0.785	0.789	0.781	0.774	
	1.00	0.688	0.685	0.677	0.668	0.641
	2.00	0.543	0.469	0.506	0.519	0.341
	3.00	0.597	0.391	0.604	0.781	0.209
	4.00	0.745	0.362	0.863	1.441	0.135
$2p\sigma-3p\sigma$	0.00					0.000
	0.25	0.047	0.047	0.030	0.030	
	0.50	0.087	0.088	0.056	0.055	
	0.75	0.118	0.119	0.076	0.074	
	1.00	0.142	0.144	0.091	0.086	
	2.00	0.215	0.220	0.174	0.147	
	3.00	0.285	0.284	0.236	0.157	
	4.00	0.353	0.333	0.305	0.150	
$2p\sigma-3d\sigma$	0.00					0.817
	0.25			0.793	0.796	0.794
	0.50			0.732	0.743	0.736
	0.75			0.670	0.694	
	1.00			0.632	0.676	0.630
	2.00			0.670	0.866	0.731
	3.00			0.713	1.118	0.948
	4.00			0.626	1.140	1.141
$2p\sigma-3s\sigma$	0.00					0.181
	0.25	0.113	0.113	0.115	0.116	
	0.50	0.010	0.009	0.017	0.017	
	0.75	-0.063	-0.065	-0.054	-0.052	
	1.00	-0.100	-0.100	-0.088	-0.085	
	2.00	-0.128	-0.104	-0.096	-0.093	
	3.00	-0.134	-0.074	-0.074	-0.089	
	4.00	-0.132	-0.038	-0.039	-0.075	
$2s\sigma-3p\sigma$	0.00					0.590
	0.25	0.707	0.709	0.705	0.704	
	0.50	0.907	0.919	0.905	0.904	
	0.75	1.081	1.112	1.087	1.084	
	1.00	1.192	1.249	1.209	1.204	
	2.00	1.276	1.464	1.328	1.320	
	3.00	1.248	1.605	1.369	1.370	
	4.00	1.245	1.806	1.385	1.361	

Table 2 (continued)

Dipole Transition Integrals.

Transition	R_{AB}	1st Order Dipole Length	1st Order Dipole Velocity	2nd Order Dipole Length	2nd Order Dipole Velocity	Exact Value
$2s\sigma-3d\sigma$	0.00					0.000
	0.25			0.040	0.040	0.040
	0.50			0.086	0.087	0.085
	0.75			0.132	0.136	0.137
	1.00			0.172	0.182	0.199
	2.00			0.222	0.306	0.343
	3.00			-0.299	0.017	0.322
	4.00			-1.164	-0.525	0.026
$2s\sigma-3s\sigma$	0.00					0.000
	0.25	0.052	0.052	0.054	0.054	
	0.50	0.106	0.107	0.112	0.112	
	0.75	0.159	0.161	0.172	0.172	
	1.00	0.208	0.212	0.231	0.231	
	2.00	0.352	0.363	0.436	0.438	
	3.00	0.431	0.451	0.564	0.572	
	4.00	0.483	0.502	0.503	0.503	
$3p\sigma-3d\sigma$	0.00					1.732
	0.25			1.732	1.734	
	0.50			1.726	1.730	
	0.75			1.705	1.710	
	1.00			1.667	1.671	
	2.00			1.314	1.357	
	3.00			0.821	0.786	
	4.00			0.347	0.217	
$3p\sigma-3s\sigma$	0.00					2.452
	0.25	2.399	2.387	2.403	2.394	
	0.50	2.221	2.224	2.235	2.229	
	0.75	1.978	1.988	2.001	1.994	
	1.00	1.761	1.771	1.789	1.780	
	2.00	1.395	1.362	1.450	1.462	
	3.00	1.412	1.306	1.649	1.771	
	4.00	1.559	1.358	2.116	2.491	
$3d\sigma-3s\sigma$	0.00					0.000
	0.25			0.058	0.059	
	0.50			0.106	0.107	
	0.75			0.134	0.136	
	1.00			0.137	0.141	
	2.00			0.019	0.033	
	3.00			-0.350	-0.347	
	4.00			-0.796	-0.843	

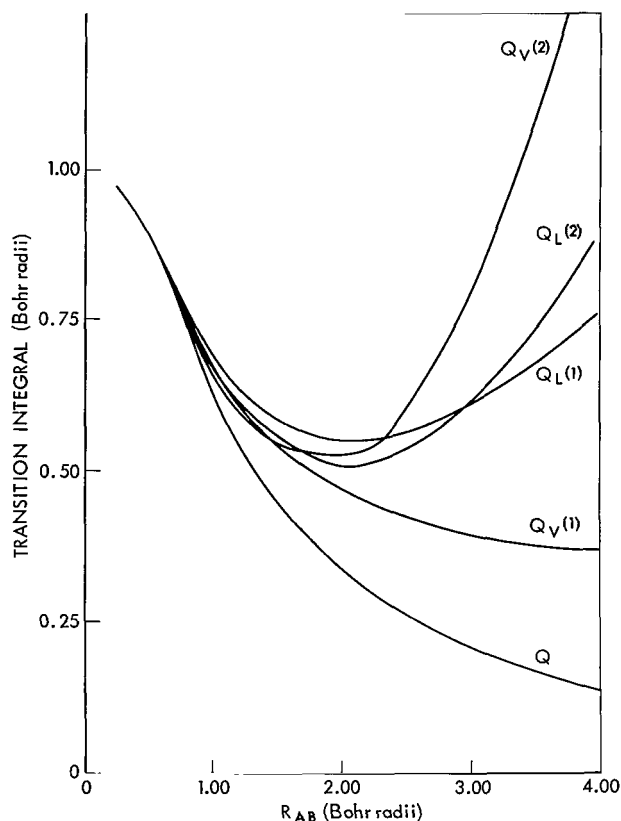


Figure 5— $2p\sigma$ - $2s\sigma$ dipole transition integral versus R_{AB} . Q is exact result, $Q_L^{(2)}$ is second-order dipole length, and $Q_V^{(1)}$ is first-order dipole velocity.

borne out by the calculations of the energy eigenvalues, the dipole moments, and some of the transition integrals. For the remaining transition integrals the situation is not clear-cut. Checking the $2p\sigma$ - $2s\sigma$ transition at $R_{AB} = 3$ and 4 in Figure 5, we find that the first-order results are superior to the second-order results. For smaller values of R_{AB} the situation reverses. Unfortunately, energy minimization is not sufficient to produce good wave functions at this level of approximation in this region. It is therefore necessary to calculate at a higher order of approximation where the potential representation will be improved. Energy minimization, the solution of the set of coupled differential equations, will include coupling from the newly added higher order terms back to the previously included terms and better wave functions will result. Hence a certain amount of caution must be

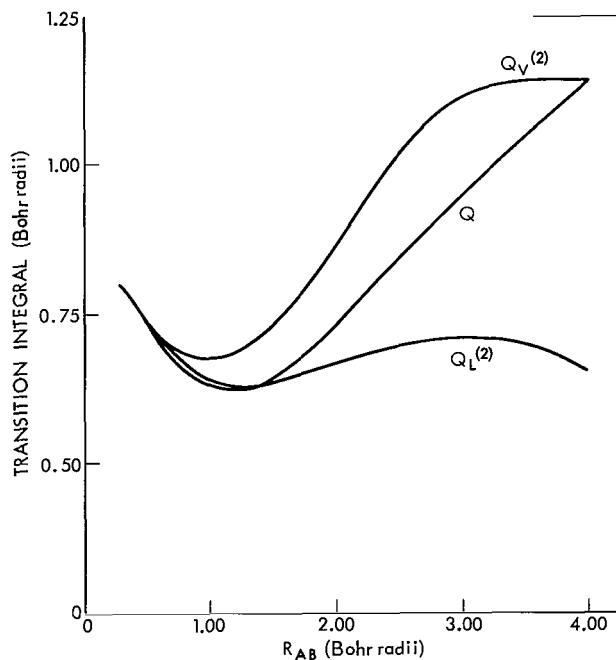


Figure 6— $2p\sigma$ - $3d\sigma$ dipole transition integral versus R_{AB} . Q is exact result, $Q_L^{(2)}$ is second-order dipole length, and $Q_V^{(2)}$ is second-order dipole velocity.

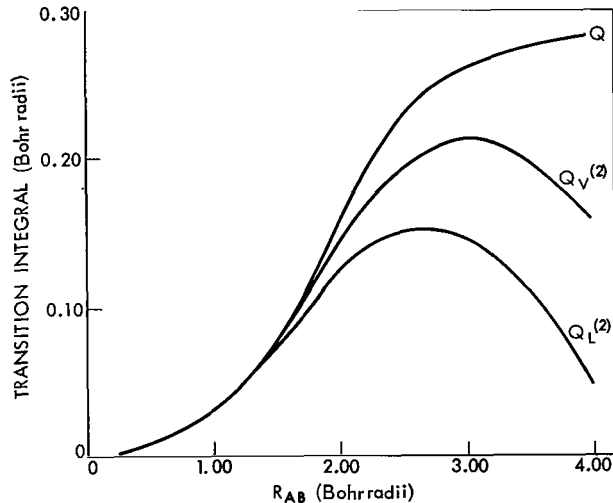


Figure 7— $1s\sigma$ - $3d\sigma$ dipole transition integral versus R_{AB} . Q is exact result, $Q_L^{(2)}$ is second-order dipole length, and $Q_V^{(2)}$ is second order dipole velocity.

Table 3

Dipole Moments.

STATE		R_{AB}						
		0.25	0.50	0.75	1.00	2.00	3.00	4.00
$1s\sigma$	First Order	0.078	0.138	0.179	0.202	0.242	0.328	0.461
	Second Order	0.078	0.137	0.172	0.186	0.157	0.162	0.214
	Exact		0.137		0.180	0.088	0.035	0.018
$2p\sigma$	First Order	-0.046	-0.110	-0.188	-0.269	-0.577	-0.953	-1.407
	Second Order	-0.041	-0.089	-0.144	-0.198	-0.400	-0.672	-1.009
	Exact		-0.092		-0.191	-0.325	-0.509	-0.657
$2s\sigma$	First Order	-0.050	-0.110	-0.180	-0.248	-0.422	-0.429	-0.326
	Second Order	-0.051	-0.124	-0.211	-0.304	-0.652	-0.801	-0.336
$3p\sigma$	First Order	0.155	0.267	0.330	0.361	0.288	-0.034	-0.528
	Second Order	0.084	0.145	0.172	0.169	0.124	-0.262	-0.772
$3d\sigma$	Second Order	0.166	0.331	0.495	0.658	1.147	1.545	1.446
$3s\sigma$	First Order	-0.254	-0.513	-0.757	-0.971	-1.466	-1.543	-1.443
	Second Order	-0.265	-0.548	-0.832	-1.102	-1.956	-2.353	-1.803

used before using values of the dipole transition integral calculated at values of R_{AB} greater than unity.

CONCLUSION

By expanding the wave function in a series of partial waves and expanding the electronic potentials in a series of Legendre polynomials, we have derived a set of coupled differential equations which describe the radial functions which are the coefficients of the partial waves in the expansion. These equations have been solved numerically using a high-speed computer. For the second-order approximation the results are accurate up to $R_{AB} = 1$. In addition the dipole moments and dipole transition integrals are also accurate up to this point. The strengths of this method are that at

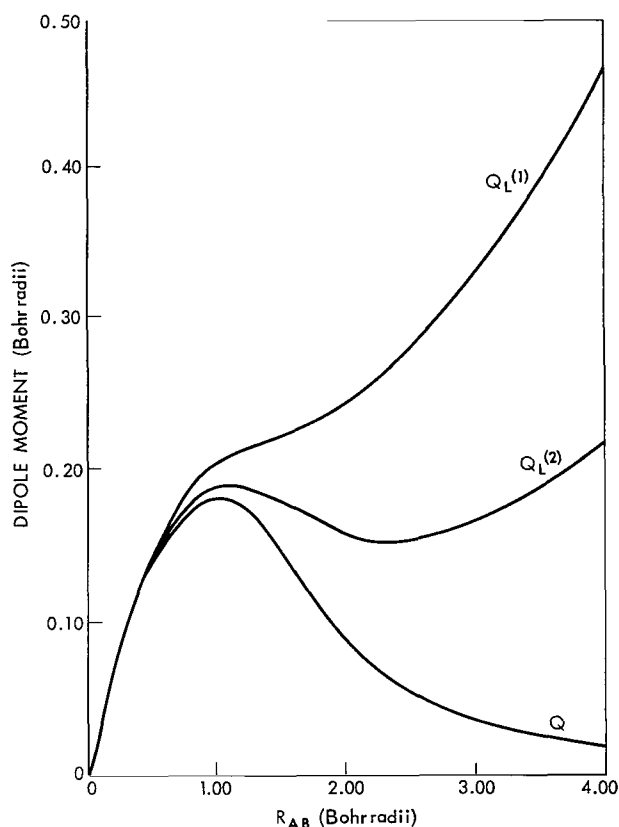


Figure 8— $1s\sigma$ dipole moment versus R_{AB} . Q is the exact result, and $Q_L^{(1)}$ is the first order dipole moment.

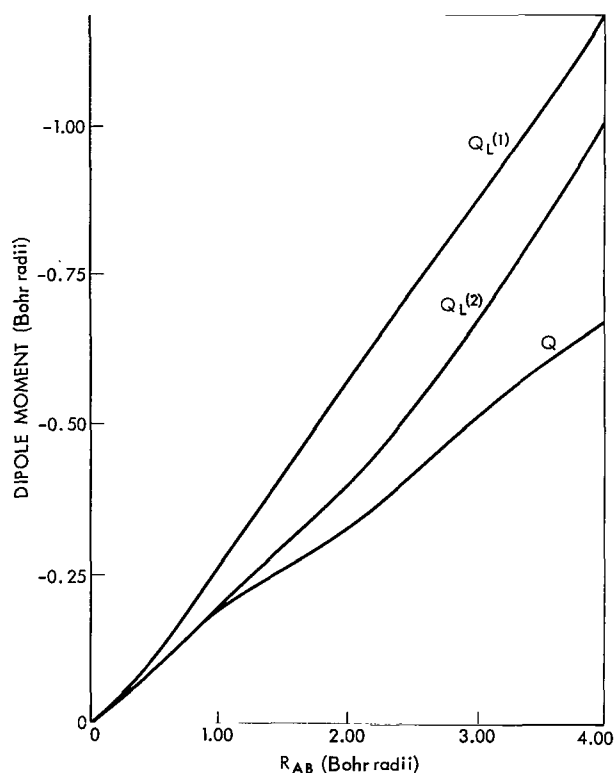


Figure 9— $2p\sigma$ dipole moment versus R_{AB} . Q is the exact result, and $Q_L^{(1)}$ is the first order dipole moment.

every order of approximation the eigenvalues are extrema and the eigenfunctions are orthogonal. Also it is possible to calculate all the eigenvalues and eigenfunctions of a given order and symmetry from the same computer program (Reference 1). The weaknesses of the method are that approximation becomes poorer as R_{AB} is increased, and in order to improve the accuracy it is necessary to calculate higher orders of the approximation.

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